# Silica polymerization. Rate constants at 23° to 80°C as a function of pH

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When monomeric silica concentration exceeds the solubility of amorphous silica monomeric silica reacts to form polymeric silica. It is generally agreed that the polymerization proceeds until the concentration of monomeric silica is equal to the solubility of amorphous silica. Much work has been done over the years to determine the rate of silica polymerization but to date there is no general agreement on rate laws. Rate orders of 1 to 8 and rate maximum between pH 6 to 9 have been reported. Part of the discrepancies is probably due to failures to recognize things like induction periods and failure to account for higher amorphous silica solubility at high pH values.

After the initial stages of silica polymerization, where silica is forming nuclei of critical size, the polymers have a tendency to maximize the number of siloxane bonds (Si-O-Si) and minimize the number uncondensed SiOH groups and they become spherical units. These polymers grow with addition of monomeric silica on their surfaces. At this stage of silica polymerization there is equilibrium between the silica polymers and monomeric silica in solution. As polymerization continues the polymers increase in size and the area, to which the monomers are added, is continuously changing affecting the polymerization rate. Silica polymerization stops when the polymers are so big that surface energy does not contribute much to the total energy of the polymers. Polymers of that size have similar solubility as amorphous silica.

In this contribution are presented the results of silica polymerization experiments in the pH range 5.66-9.18 at 23°, 2.48-8.50 at 58° and 2.18-8.75 at 80°C. Ionic strength was 0.11±0.02M in all cases. Rate of silica polymerization was monitored by analyzing concentration of molybdate active silica. Results indicate that the rate of silica polymerization is greatly affected by the pH value of the solution and there is no maximum in polymerization rates over the pH range of this study. The calculated rate constants increase with rising pH value over the whole pH range of the experiments at all experimental temperatures.

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# The sulphur isotopic evolution of late Neoarchean and early Paleoproterozoic seawater

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Despite its well accepted importance for reconstructing the redox evolution of Earth’s ocean-atmosphere system, our knowledge of the abundance and isotopic composition of seawater sulphate decreases substantially with increasing time. This is most apparent for the Precambrian. In particular, the proposed rise in atmospheric oxygen abundance (Great Oxidation Event) around 2.3 Ga ago and an assumed parallel increase in the abundance of dissolved oceanic sulphate is not documented at all.

Here, we report abundances for sulphate sulphur as well as sulphur and oxygen isotopic compositions for the Neoarchean-Paleoproterozoic succession deposited on the Kaapvaal Craton between 2.65 and 1.92 Ga, i.e. the Transvaal Supergroup of eastern Transvaal and correlative units in the Griqualand West Subbasin.

Trace sulphate extracted from 16 carbonates of the Koegas, Duitschland, Mooidrai, Silverton and Lucknow formations gradually increase from less than 0.1 to 23.5mmol/kg. The respective sulphate sulphur isotopic composition varies between +4.6 and +34.6‰ with a distinct stratigraphic trend being discernible. The oxygen isotope values for the trace sulphate displays a range between +6.1 to +21.1‰.

Individual stratigraphic units are well constrained in their isotopic composition. Yet, the truly global significance of the isotope record needs to be verified with additional analyses. So far, respective host carbonates have provided a carbonate carbon isotopic composition that includes pertinent features considered characteristic for this time interval, such as the globally recorded $^{13}$C maximum (the Lomagundi-Jatulian event).

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